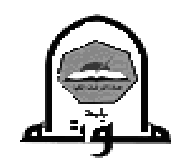


Mu'tah University
Deanship of Graduate Studies

Synthesis of Thia and Amino Podands with Lipophilic Ester End Groups and Their Applications in Determination of Some Rare Metals

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This thesis has been submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, Department Of Chemistry

Mu'tah University, 2012

Dedication

I can not find the words that can express my gratitude to my dear husband Ma'un Tawara for his patience, sympathy, caring, and supporting through out this research project and there is no doubt in my mind that without his continued suppot and counsel I could not have completed this thesis,so , firstly I dedicate this thesis for him.

I'm grateful to all my family and friends for their support that they give me when it in need.

Muna A. H. Al-Ni'mat

ACKNOWLEDGMENT

In the beginning, my thanks, deepest gratitude, and sincere apperciation to Associated prof.Waleed Manasreh and Professor. Mohammad Al-Ashram for their supervision, help, support, and continuous encouragement along this research work.

Thanks also to Professor. Kamal Al-Momani, Professor. Mohammad Zaitoun and Dr. Fadel Al-Wedyan, as members of examining committee for their valuble suggestions and comments.

Also, many thanks for chemistry department in Mu'tah university and Alhussein bin Talal university.

Finally, many thanks for all those who support me in this reasearch product.

Muna A. H. Al-Ni'mat

Table of contents

List of Table

List of Figures

List of Abbreviations

AAS	……….	Atomic Absorption Spectroscopy
C_o	……….	Initial Concentration
C_f	……….	Final Concentration
C_R	……….	Removal Concentration
C T	……….	Contact time
g	……….	Gram
h	………..	Hour
L	……….	Ligand
min	……….	minute
ppm	………..	Parts per million
Q	………..	Adsorptive capacity
R_{em} %	………..	Percentage removal

List of Appendix

Abstract

Synthesis of Thia and Amino Podands with Lipophilic Ester End Groups and Their Applications in Determination of Some Rare Metals

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Method was applied to coat Whatman No. 1 filter paper with podands **3** and **4** and dried at different temperatures (25, 50, 80 ^{o}C), which did not give a significant difference in the complexation results for each podand. Also a modified method of literature was applied to extract heavy metals as a complex with podand **5** from aqueous layer, by immiscible organic solvent. While water-insoluble solid podands **1** and **2** were mixed and stirring with the solutions of heavy metals followed by filtration to obtain the remaining solution of the heavy metals. Studying podands complexation with some heavy metals: UO_2^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} and Hg^{2+} was done as a function of pH and contact time, by using conductivity for uranyl cation and AAS for the others, to determine their ability to metal adsorption by calculating the Adsorptive capacity Q (mg metal / g adsorpent), and Percentage removal (R_{em}) of heavy metal. Results show that, at low pH (4.13) the adsorption of heavy metals was less than at high pH (8).

Suitable contact time to obtain maximum complexation was about 4h. The results showed that Hg^{2+} and Cu^{2+} were the highest adsorbed cations; Zn^{2+} and Ni^{2+} were moditately adsorbed cations; while, Co^{2+} and $UO2^{2+}$ were the lowest adsorbed cations.

الملخص

تحضير المتشكلات شبه الحلقية الثيولية والأمينية ذات المجموعة الإسترية الطرفية الرابطة للدهن، وتطبيقاتها في تحديد بعض الفلزات النادرة

منى النعيمات

جامعة مؤتة، 2012

طبقت طريقة طلاء لورقة ترشيح واتمان رقم 1 مع المتشكلات رقم 3 و 4 ثم جففت عند درجات حرارة مختلفة (25 ،50، 80) س^{o} ، والتي لم تعطي اختلاف ملحوظ في نتائج المركبات المعقدة لكل متشكلة. أيضا طبقت طريقة معدلة لاستخلاص المعادن الثقيلة على شكل معقدات بوجود متشكلة 5 من الطبقة المائية باستخدام مذيب عضوي غير قابل للامتزاج. بينما المتشكلات 1، 2 الصلبة عديمة الذوبان بالماء مزجت وحركت مع محاليل العناصر الثقيلة ثم رشحت للحصول على الراشح للمعادن الثقيلة. تم دراسة معقدات هذه المتشكلات شبه الحلقية مع بعض العناصر الثقيلة Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{+2}, UO_2^{+2} و Hg^{2+} كعلاقة مع درجة الحموضة وزمن التحريك. تم استخدام مبدأ الموصلية لأيون UO_2^{2+} وجهاز طيف الامتصاص الذري لبقية المعادن لتحديد قابلية المتشكلات شبه الحلقية على عمل امتزاز لها من خلال حساب القدرة الامتزازية (السعة الامتزازية) ونسبة الإزالة للأيونات الموجبة للعناصر الثقيلة عند درجة حموضة منخفضة (4.13) .

أظهرت النتائج أن امتزاز العناصر الثقيلة كان أقل عند درجة حموضة (4.13) منه عند درجة حموضة مرتفعة (8).

كما كان لزمن المزج دورا في الحصول على اعلى نسبة في عملية تشكيل المعقد وهو 4 ساعات.

كذلك بينت النتائج أن الايونات، Cu^{2+} و Hg^{2+} كانتا الأكثر امتزازا ، يليها Zn^{2+} وNi^{2+} ، أما UO_2^{2+} وCo^{2+} فكانت الأقل.

Chapter One
Theoretical Background

1.1. Complexation and Complex compounds

Complexation can actually be defined as a simple interaction between a donor (ligand) and an acceptor (substrate). Complex formation may happen according to the three routes of distinctive, selective, or specific complexation. In a distinctive complexation, the ligand (L) tends to form complexes with substrates, which means that thermodynamic and kinetic effects between L and all substrates are identical and hence all K_f values are equal. Selective complexation: the ligand prefers one of the substrates over the others and has a higher tendency to form a complex with it. While in the specific complexation, on the other hand, L forms a complex with only one of the substrates (Toyota, Sekizaki, Takahashi, Kunihiko and Tanizawa, 2005).

A metal complex or coordination compound is a compound formed from a Lewis acid and a Brønsted base, a Lewis acid is an electron pair acceptor and a Brønsted base a proton acceptor. (Wilkinson, Gillard and McCleverty, 1987).

Coordination chemistry of podands and absorbants plays an important role in purification of wastewater from toxic heavy metals, and extraction the heavy metals from ore salt solution. Toxic heavy metals in air, soil and water are global problems that are growing threat to the environment. Therefore, the removal and separation of toxic and environmentally relevant heavy metal ions are a technological challenge with respect to industrial and environmental applications (Trivunac and Stevanovic, 2006). The removal processes of heavy metals from natural water and contaminated solvents by heavy metal ions are attractive for environment. A series of approaches can be applied to metal ion removal from water based on precipitation, exchange resins, membrane filtration and adsorbing methods (Kursunlu, Guler, Dumrul, Kocyigit and Gubbuk, 2009). A promising process for the removal of heavy metal ions from aqueous solutions involves bonding the metals to a bonding agent, such as macromolecular species, and then separating the loaded agents from wastewater by separation processes such as membrane filtration. (Trivunac and Stevanovic, 2006) water soluble ligand (Trivunac and Stevanovic, 2006.; Barakat, 2008), or insoluble are suitable for this action (Wing, Doane and Russell, 1975.; Kim and Lee, 1999).

The complexation –ultrafiltration proccess has been successfully applied for removal of Cu(II), Ni(II), and Cr(III) ions from synthetic wastewater solutions with good result in neutral and alkaline conditions than in acidic one (Barakat, 2008.; Barakat and Schmidt, 2008). UO_2^{2+} removal by organic matter was also reported (Semiao, Rossiter and

Schafer, 2010). The advantages of complexation-filtration process are the high separation selectivity due to the use of a selective binding and low-energy requiements involved in these proccesses.

1.2 . Heavy metals

Heavy metals are defined as those having a specific density of more than 5 g/ml (Järup, 2003). They are dangerous because they tend to bioaccumulate. The bioaccumulation is an increase in the concentration of a chemical species in a biological organism over time, and the are stored faster than they are metabolized or excreted. Heavy metals can not be degraded or destroyed. They can enter our bodies to a small extent via food, drinking water and air (Abu Bakar, 2008).

Emission of heavy metals to the enviroment occurs via a wide range of processes and bathways, including to the air, during combustion, extraction and proccesing, to surface water, via runoff and releases from storage and transport, and to the soil via irrigation of plants (Järup, 2003.; Singh, Sharma, Agrawal and Marshall, 2010). This emission affects on the human and organisims life (Dietrich, 1998; Singh, Sharma, Agrawal and Marshall, 2010).

Heavy metals have been used in different areas, for example; mercury is still used in gold mining in many parts of Latin America. Arsenic is still common in wood preservatives, and tetraethyl lead remains a common additives to petrol, although this use has decreased in the developed countries (Järup, 2003).

Heavy metals can be quantitatively adsorbed as metal oxides from aqueous solutions and are employed in metal preconcentration and metal removal (Luisa, Arnal and Guardia, 2003.; Hui, Chao and Kot, 2005). In order to facilitate wastewater remediation and to reduce the amount of dangerous wastes containing metal ions, different types of sorbents have been proposed, like clays, seaweed, dead biomass, (Cervera, Arnal and Guardia, 2003), zeolites (Hui, Chao and Kot, 2005), bone ash and wood (Chojnacka and Michala, 2009), calcined phosphate (Aklil, Mouflih and Sebti, 2004), alumina and chitosan (Cervera, Arnal and Guardia, 2003), and cement kiln dust (CKD) (Waly, Dakroury, El-Sayed and El-Salam, 2010).

The adsorptive capacity (mg metal / g adsorbent), Q, was evaluated using the following expression (Jimoh, Egila, Dauda and Iyaka, 2011).

$Q = ((C_o – C_e)/ m) * V$

and removal efficiency $=(C_o – C_e / C_o)* 100\%$

Where, Q is adsorptive capacity, C_o is the initial metal ion concentration (ppm), C_e the equilibrium metal ion concentration (ppm), V

the volume of the aqueous phase in Liters, and m the amount of adsorbent (g) (Hui, Chao and Kot, 2005.; Zhou, Xue and Jiang, 2011).

1.3 . Ligands

Ligands are neutral molecules or ions that attach to a central metal ion, or they are the Brønsted bases attached to a metal ion (Cotton, Wilkinson and Murillo, 1999.; Miessler and Tarr, 1999). These may be simple ions such as Cl^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ or N $(CH_2CH_2NH_2)_3$, or even macromolecules, such as proteins. The donor atom associated with the ligands supplies lone pair of electrons to the central metal atom, forming dative bonds which may be one or two more. Monodentate, one donor atom, bidentate, two donor atom,(Fig 1), tridentate, three donor atoms, (Fig 2), and if there several donor atoms are present in a single ligand as with $N(CH_2CH_2NH_2)_3$, the ligand is said to be polydentate, (Fig 3 and Fig 4).

When polydentate ligands bind to the central metal ion they form a ring called chelate and the ligand is referred as chelating agent. Ambidentate ligand is a ligand which possesses two donor atoms but in forming complex it utilizes only one atom depending upon the conditions and type of complex, examples include NO (nitro) , ONO (nitrito), CN (cyano), NC (isocyano), SCN (thiocyanide), NCS (isothiocyanide). Π- acid ligand is a Ligand which is capable of accepting an appreciable amount of π–e– density from the metal atom into emptying π or π* orbital eg. CO.

A huge variety of ligands appear in coordination complexes, and to illustrate this point, some examples of common types of ligand are shown in (Fig 1-4). Any of a variety of elements may function as donor atoms towards metal ions, but the most commonly encountered are nitrogen, phosphorus, oxygen, sulfur and the halides. In addition, a large number of compounds are known to have carbon donor atoms; these are known as organometallic compounds. Bidentate ligands may be classified according to the number of atoms in the ligand which separate the donor atoms Fig (1) and hence the size of the chelate ring formed with the metal ion. Thus 1,1-ligands form a four-membered chelate ring when bound to a metal ion, 1,2-ligands a five membered ring, and so on. Cyclic compounds contain donor atoms oriented so that they can bind to a metal ion and which are large enough to encircle. They are known as macrocyclic proligands. Bicyclic proligands can completely encapsulate a metal ion like porphine, which reflect their ability to wrap up and entomb the metal ion. Sometimes, ligands can bind to more than one metal ion in a bridging arrangement, for example in $[W_2Cl_9]^{3-}$ illustrated in (Fig 4). Certain polydentate ligands are particularly good at linking together several metal ions and are refered to as polynucleating ligands (Huheey, Keiter and Keiter, 1993).

1.4. Research Objective

The main objective of this work is to study the ability of some synthesized podands to detect some metals by different analytical methods as a function of pH and contact time, several methods were employed to study the metal detection; coating of filter paper, direct mixing with strring, and extraction by water immiscible organic solvent.

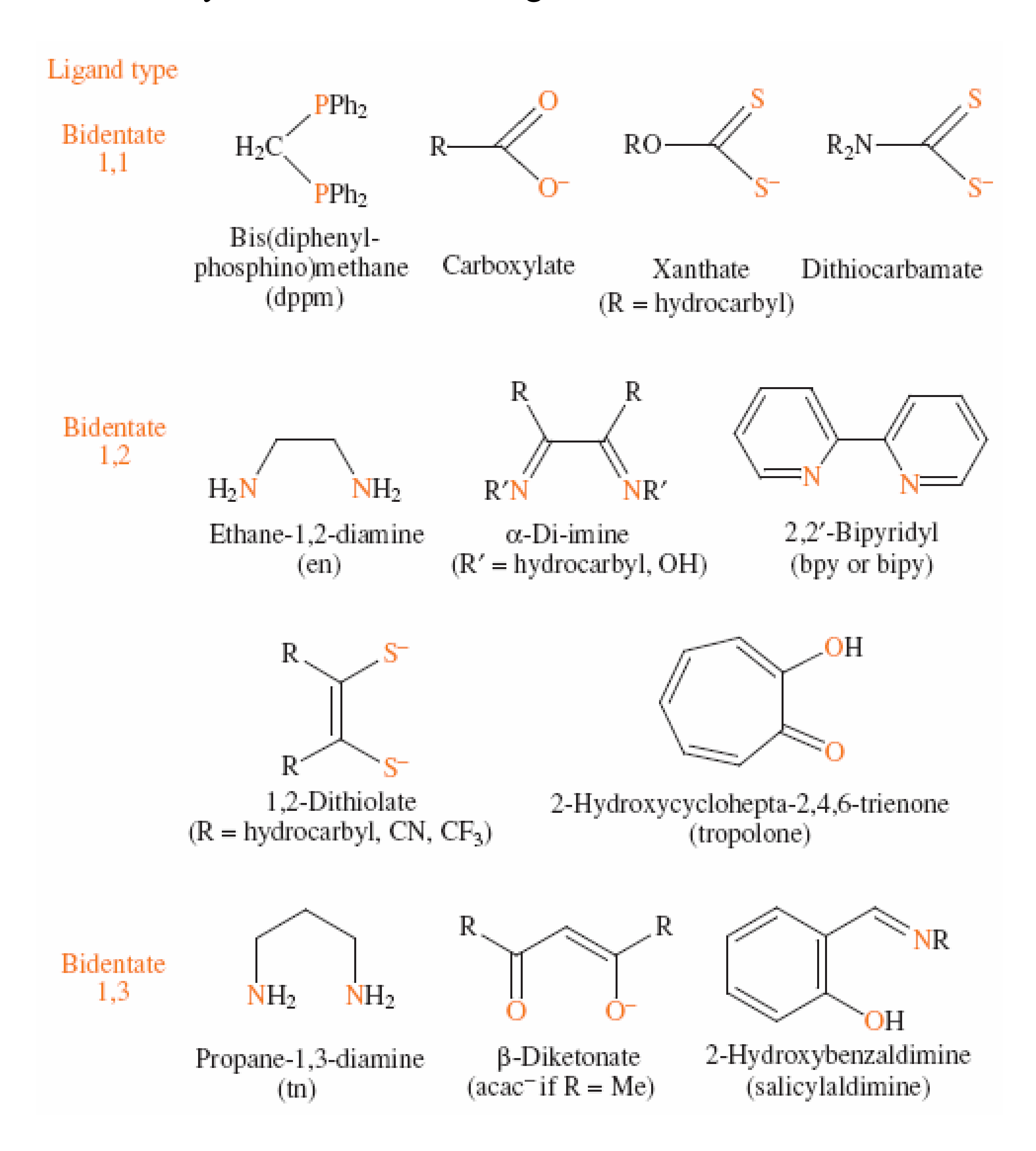


Fig 1: Examples of bidentate ligands

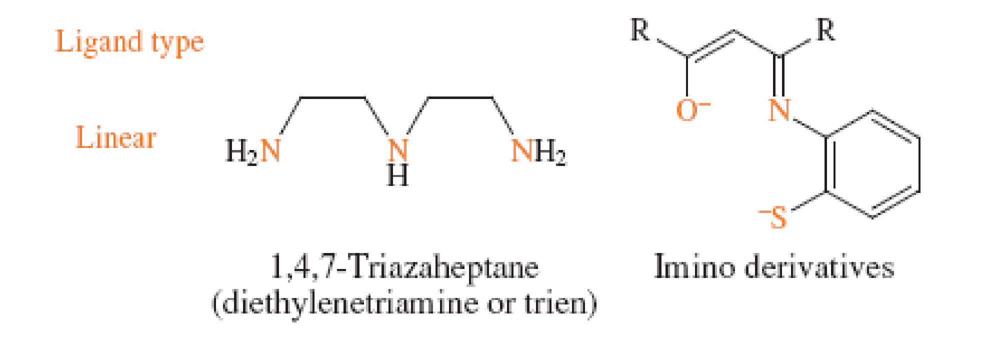


Fig 2 : Examples of tridentate ligands

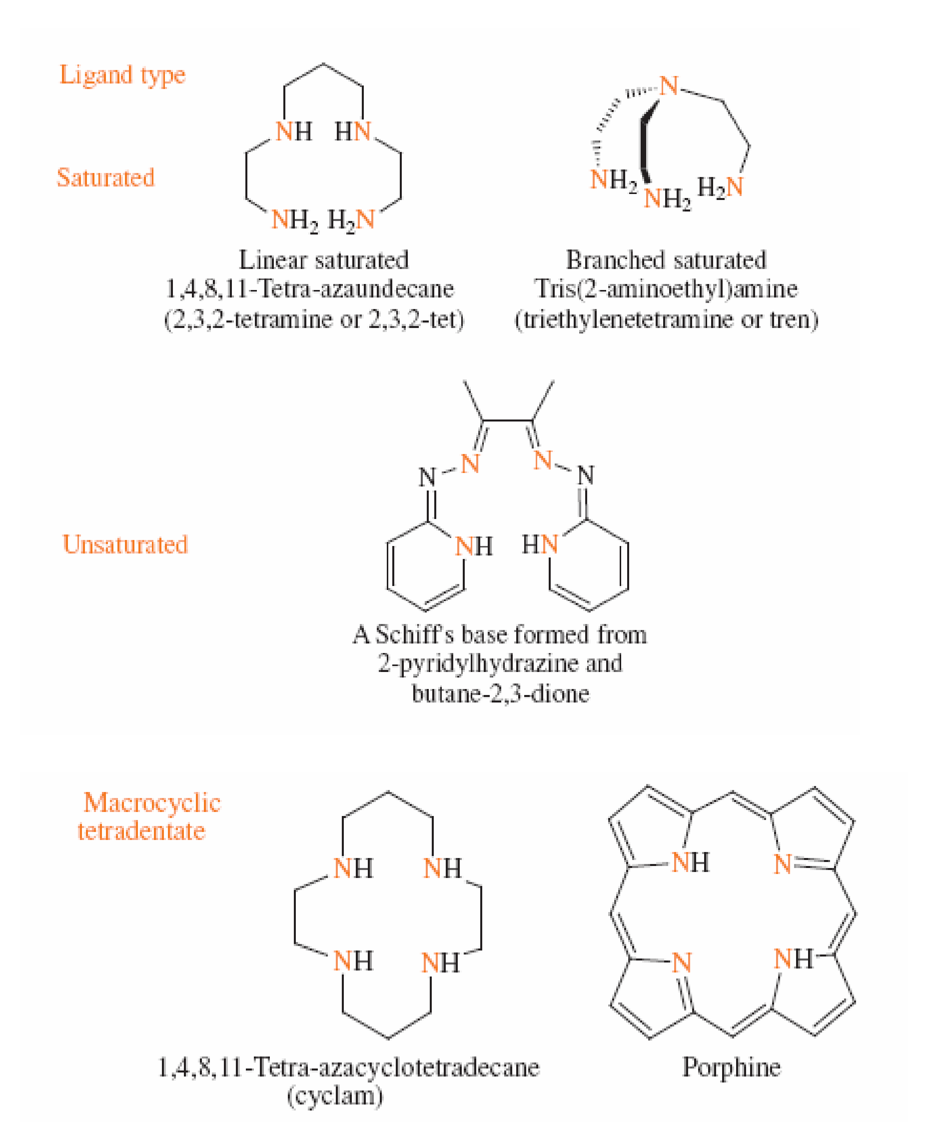


Fig 3 : Examples of quadridentate and macrocyclic ligands

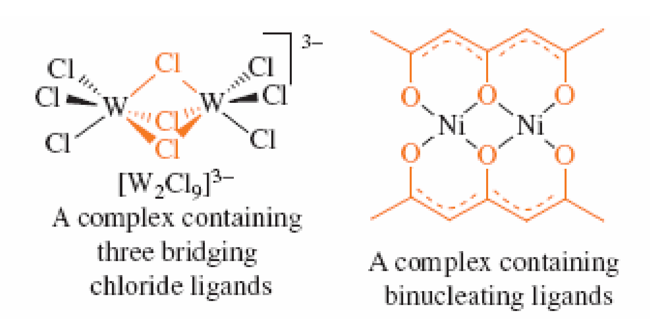


Fig 4 : Examples of a bridging ligand and a polynucleating ligand

Chapter Two
Review of Literature

2.1. Podands

The term "podands" has appeared in the chemical literature comparatively recently—towards the end of the 1970s. The name comes from the Greek word "podos"—foot, It embraces various types of acyclic polyether complex-forming agents (Kron and Tsvetkov, 1990). Podands are noncyclic multidentate ligands (Mizyed and Ashram, 2011.; Shahrisa and Banaei, 2001), also chain analogs of crown ethers are called podands (Dmitrieva, Churakova, Vedernikov and Gromov, 2004) Fig (5). They are linear or branching chain species with two or more sets of guest-binding functional groups positioned on the spacer unit in such a way as to chelate a target guest species to maximize guest affinity.

To enhance their complexing abilities and their selectivity toward a variety of metal ions, a large number of podands with different end groups and chain lengths were synthesized. podands are generally considered as poor ionophores for alkali metal cations due to their low binding affinities (Jeong, Cho, and Pyun, 1995), and form complexes with smaller stability constants than those of corresponding macrocyclic complexes and thus are usually regarded as poor ligands (Shahrisa and Banaei, 2001.; Iimori. and Still, 1989), compared with the corresponding cyclic analogues such as crown ethers. This problem can be tackled by forcing the conformations of podands preorganized to be semi-cyclic or cyclic. It may be accomplished by exploiting intramolecular interactions between two terminal groups of podand hosts (Jeong, Cho, and Pyun, 1995). Unsymmetrical ligands can be prepared, and their complexes with certain metals such as copper which play an important role in the bio-system. (Gilbert, Addison, Nazarenko and Butcher, 2001).

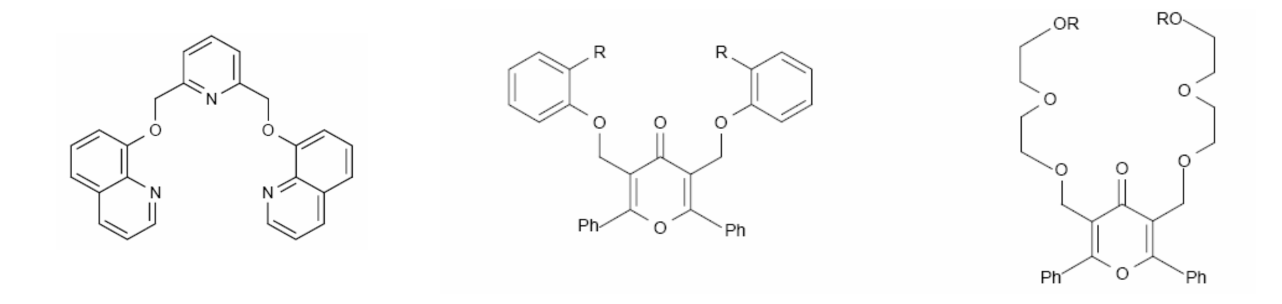


Fig 5: Examples of podands

2.2. Schiff's base podands

Schiff's bases are considered "privileged ligands" which formed as a result of condensations of primary amines and aldehydes or ketones, RCH=NR′, where R and R′ representes alkyl and / or aryl substituents (Kumar, Dhar and Saxena, 2009) Fig (6).

Symmetrical bis-Schiff bases derived from one mole of the diamine and two mole of the same type of aldehydes/ketones. Unsymmetrical bis-Schiff bases derived from one mole the diamine and two different aldehydes/ketones. They are more difficult to obtain by displacement reactions of 1 mole of symmetrical bis-Schiff bases with 1 mole of different type of aldehyde or ketone under reflux in 95% ethanol (Tan and Ang, 1988).

These ligands have been extensively studied in coordination chemistry, and are found to be stable under a variety of oxidative and reductive conditions (Singh, Gupta and Gupta, 2007). Schiff's bases are actually able to stabilize many different metals in various oxidation states (Toyota, Sekizaki, Takahashi, Kunihiko and Tanizawa, 2005).

Schiff's base podands have the potential to be used in different areas such as electrochemistry, bioinorganic, separation processes and environmental chemistry (Shemirani, Mirroshandel, Salavati-Niasari, Kozani, 2004). Schiff's base podands and their metal complexes as catalysts in various biological systems (Canpolat and Kaya, 2005.; Kumar, Dhar and Saxena, 2009), polymers , dyes, antifertilityand enzymatic activity (Kumar, Dhar and Saxena, 2009), material in solid phase extraction (Naeimi, Safari and Heidarnezhad, 2007), analytical and pharmacological areas (Raman, Raja and Sakthivel, 2007). Amido-Schiff base forms chelates with Cu(II) and Fe(II) and acts as thrombine inhibitor (Toyota, Sekizaki, Takahashi, Kunihiko and Tanizawa, 2005).

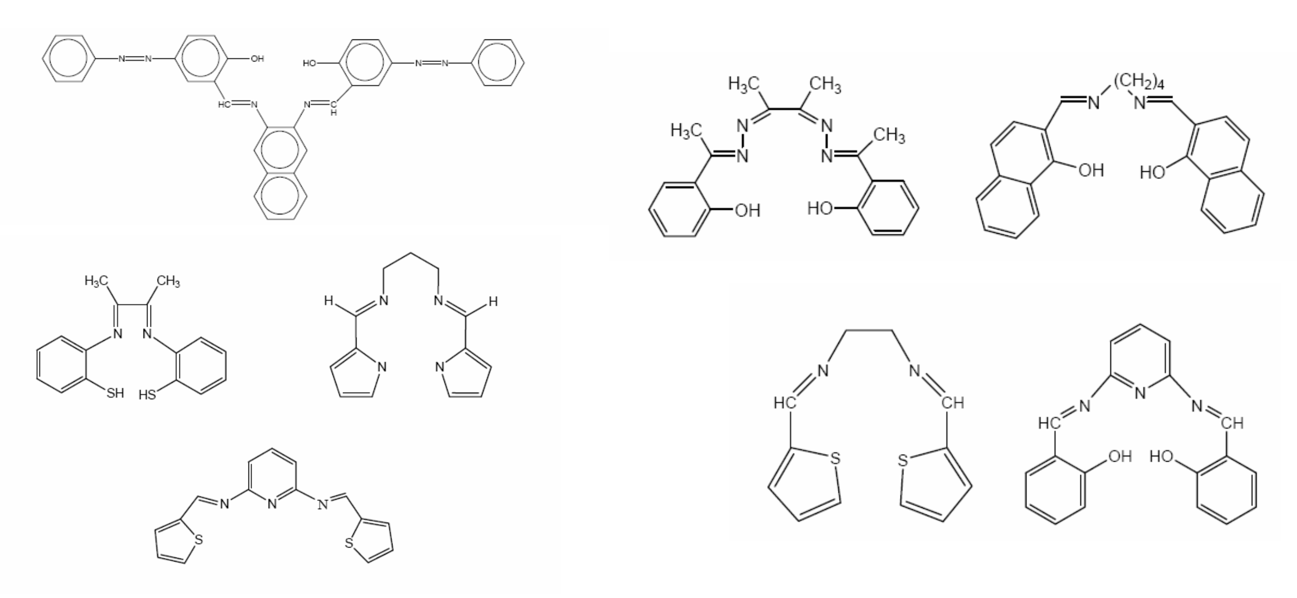


Fig 6: Examples of Schiff's base podands

Chapter Three
Design and Methodology

3 . 1 . Materials and Equipments :

Salicylaldehyde, Bromoethylacetate, Ethandithiol, 2-Mercaptoethyl sulfide, 2-Mercaptoethyl ether, Ethylenediamine, Sodium borohydride, Chloroacetylchloride, Diethyleneamine, Potassium iodide, Potassium carbonate anhydrous, Magnesium sulfate anhydrous and Whatman No 1, 7.0 cm were purchased from Aldrich Company. Thionyl chloride and Sodium hydroxide were purchased from Laboratory Rasoyan Company.

The salts : $HgCl_2$ was purchased from VWR Company, $Cu(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$, $UO_2(NO_3)_2.6H_2O$, $Zn(NO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ were purchased from Aldrich Company.

The solvents : Ethanol 99.9% , Acetonitril 99.9% , Dichloromethane 99.9% , Diethyl ether anhydrous, Cyclohexane, Ethyl acetate and Acetone anhydrous were purchased from Tedia Company.

Eutech instrument pc510 - pH/conductivity/TDS/C^o/F^o meter for conductivity experiments and pH adjustment. Thermo scientific deionizer model No D7031 for deionised water. Metal cations were analyzed using flame atomic absorption spectrophotometer (AAS novAA300, analytik jena).

3.2 . Starting Materials :

o-(Ethoxycarbonyl- methoxy)benzaldehyde was prepared as literature (Ashram, 2002). 2-chloro-N,N-diethylacetamide, o-(N,N-diethylcarbonylmethoxy benzaldehyde**),** o-(Ethoxycarbonylmethoxy) benzyl alcohol and o-(Ethoxycarbonyl methoxy)benzyl chloride were prepared as literature (Mizyed and Ashram, 2011).

3.3 . Preparation of *Podands*, 1 , 5 by Schiff's base reaction.

Schiff's base podands 1 , 5 were prepared as literatures (Ha, Ong, Win, Koh and Yeap, 2008.; Tan and Ang, 1988.; Naeimi, Safari and Heidarnezhad, 2007.; Raman, Raja and Sakthivel, 2007.; Mizyed and Ashram, 2011).

3.4 . Preparation of final products *(Podands)*. 2 , 3 , 4 .

Podands 2, 3, 4 were prepared as literature (Ashram, 2002).

3.5. Complexation Study .

3.5.1. Coating Compound <u>3</u> and <u>4</u> on filter paper.

Compound **<u>3</u>** and **<u>4</u>** were dissolved separately in about 10 ml of acetone in two plastic petrri dishs. Three weighed cleaned filter papers (Whatman No 1, 7.0 cm) were immersed in this solution for 5 min, and dried at different temperaturs (25, 50 and 80 ^oC). The filter papers were then reweighed to calculate the mass of the podand which was between 0.072-0.076 g. (Ackerman and Hurtubise. 2002).

3.5.2 . Preparation of Metal Solutions.

For each heavy metal, a stock solutions of (1L, 40 ppm) were prepared and then diluted to (50 ml, 8 ppm). The pH 4.13 and 8.0 which was adjusted using 0.1M HCl and 0.1 M NaOH solutions (Chojnacka and Michala;, 2009.; Aklil, Mouflih and Sebti, 2004.; Barakat and Schmidt, 2008), and then kept in plastic volumetric flasks.

3.5.3 . Synthesis of complexes.

Standard solutions with concentrations (1.0 , 3.0 , 5.0 , 7.0 , 10) ppm were prepared for each of the following metals: (Zn^{2+} , Cu^{2+} , Co^{2+} , Hg^{2+} , Ni^{2+} , UO_2^{2+}) to builed up the calibration curves at two pH values: 4.13 and 8.0, pH values of 4.13 and 6.7 were used for Cu^{2+}.

3.5.3.1- Solid Podands, <u>1</u> and **<u>2</u>** .

The sorption was performed in an aqueous solution for divalent (zinc, copper, cobalt, mercury, nickel and uranyl) nitrates or chlorides, at 25 ±1 C^o. A 85.0 mg of solid podands were suspended in 50.0 mL of aqueous solution containing (50mL, 8 ppm) of each cation in 100 mL plastic Erlenmeyer flask, for a period of time (4, 8, 24, 48) hours, and at different pH values. At the end of the time period, the suspension was filtered and the remaining cations in the solutions were determined by AAS and conductivity was measured for uranium. (Cervera, Arnal and Guardia, 2003.; Raman, Raja and Sakthivel, 2007.; Kursunlu, Guler, Dumrul, Kocyigit and Gubbuk, 2009.; Tan and Ang, 1988).

3.5.3.2. Coated filters with Podands, <u>3</u> and <u>4</u>.

Using a plastic Buchner funnel, a solution of each heavy metal (50 mL, 8 ppm) in a different pH values was filtered over using a coated filter papers with a compound 3 and 4 which was placed above another uncoated filter paper, the filtrate of metallic cations then determined by AAS, while uranium was determined by a conductivity meter. (Ackerman and Hurtubise. 2002).

3.5.3.3. Semi-Solid Podands, 5 .

A 85.0 mg of solid podand and 5 mL of CH_3CN were added into 50.0 cm^3 volumetric flasks containing 8 ppm of each cation at different pH values. Each mixture then transfered to 100 mL plastic erlenmeyer flask and left to stir for a period of time (4, 8, 24, 48) hours. At the end of the time period, two portions of 20 mL of CH_2Cl_2 were added to the solution to extract the complexes. The remaining cations in aqueous layer were determined by AAS. While uranium was determined by a conductivity meter (Cervera, Arnal and Guardia, 2003).

Chapter Four
Results, Discussion and Recommendations

Our work deals with two parts, the first one is the preparation of podands, and the second is studying their complexation abilities with cations: UO_2^{2+}, Zn^{2+}, Cu^{2+} , Co^{2+} , Ni^{2+} and Hg^{2+}

.

4.1. Complexation study

In principle, complexation can be followed by heat of reaction, change in color, NMR chemical shifts or conductance (Ashram, Bqaeen and Mizyed, 2010). In our work, the effect of pH and contact time on complexation process were studied. Conductivity measurements can be a useful tools for investigation the complexation process. (Shahrisa and Banaei, 2001), which we applied here for uranyl ion. In every case, it was observed a gradual decrease in the conductance by mixing the ions with podands. This behavior indicates that the complexed metal ions are less mobile than the corresponding solvated M^{2+} ions (Ghasemi and Shamsipur, 1996). Other metals were determined by AAS Spectrometry.

If the impurities are in the ionic or complex forms, then the extraction of the organic compounds in a suitable organic solvent with aqueous acidic or alkaline solutions will reduce their concentrations to acceptable levels. That means: liquid, semi solid, or solid podands can be used directely, by dissolving them in a immiscible-water organic solvent, then added to a solution contains metal cations to extract it as a complex with organic solvents. Then the remaining concentrations of cations can be measured.

However, podands are generally considered poor ligands compared with those of corresponding macrocyclic ligands (Mizyed and Ashram, 2011). Due to their high degree of flexibility and increased number of donating atoms in the macrocyclic ring, they can warp themselves around the metal ions of proper size to form tridimensional “waro around” complexes. In which all donating atoms of the ring are coordinating to the central cation (Pourghobadi et al, 2000). Selectivity of the interaction with heavy metals, when N,O-macrocyclic reagents are used, is determined not only by the size of the cavity but also by the conformational mobility of the molecule as a whole. The presence of C=N double bonds in Schiff’s base podand makes the molecule of substantially more rigid, while macrocycles which contain C—N bond is distinguished by a higher conformational mobility (Zolotov Yu. A. Malofeeva G. I. Petrukhin O.M. and Timerbaev A.R, 1987).

All data are illustrated in Fig . 7 - 18 and Tables 2 – 12. According to Q and Rem, values in fig . 17, fig . 18 and table 2 show the best podand for each studied heavy metal. Table 3 shows heavy metal that detected at

high level by each used podand. For example, uranyl cation was detected efficiently by podand 4 , while podand 4 detected mercury cation efficiently from the set of studied heavy metals.

As shown in table 2, the order of the detection of metal cations with podands 1-5 was: Podand 1 / Hg2+ > Zn2+ > Cu2+ > Ni2+ > Co2+ > UO22+ . Podand 2 / Hg2+ > Cu2+ > Zn2+ > Co2+ > Ni2+ > UO22+ . Podand 3 / Hg2+ > Cu2+ > Zn2+ > Ni2+ > Co2+ > UO22+ . Podand 4 / Hg2+ > Cu2+ > Zn2+ > Ni2+ > UO22+ > Co2+ . Podand 5 / Hg2+ > Zn2+ > Ni2+ > Cu2+ > Co2+ > UO22+ . Which mean Hg2+ and Zn2+ were the highest detected cations, Cu2+ and Ni2+ were moderate detected cations, Co2+ and UO22+ were lowest detected cations.

The lowest Q value is zero, but the highest one is varied, because Q values are depending on the Co, Cf, volume of solution sample and the mass of podand, by contrast, the range values of Rem is from 0.00% - 100.00%. therefore, in our study, the maximum Q value for podands 1, 2 and 5 was 4.71 ± 0.09, when Cf is zero ppm. And minimum Q value always was zero when Cf equal Co which in our study was 8ppm. In case of coated podands 3 and 4, the maximum Q value was 5.26 ± 0.08, the difference between the two maximum Q values related to the used mass of podands 1, 2 and 5 was 85 mg, while 76 mg was for podands 3 and 4.

According to Fig.17 and Fig.18, we notic that the best podand for each cation. For UO22+, podand 4 was the best, this may be due to the large size of this podand and presence of oxygen atom in bridge group.For Zn2+ and Ni2+, the best podand was podand 5, and this may be due to the small size of inter space of podand, also, Zn2+ and Ni2+ are hard cations, which have stronger interaction with nitrogen atom of bridge group and amide group. While the podand 2 was the best for Cu2+ and Hg2+ , this may explained that Cu2+ and Hg2+ are soft cations, which have stronger interaction with sulfur atom in addition of small size of inter space of podand, which means that the distance between the cations-sulfur is more close together.

4.2. Effect of pH

The effect of pH value was investigated at pH 4.13 and 8.0 with fixed metal concentration at 8 ppm, to achieves the rejection of cations with podands 1-5 in acidic and alkaline mediums, above pH 8.0, ~> 8.4, was not suitable because all cations precipitated as hydroxide except Cu2+ which was studied at pH 6.7 instead of pH 8.0. The rejection of metal ions at the two pH values are shown: Table (3), illustrates the Cf of metals solution at two pH values 4.13 and 8.00 for podand 1, we notice that the Cf is less than Cf at pH 4.13, which the same notice in tables (5, 7-11) for podands 2, 3, 4 and 5 respectively. Fig (7) shows the maximum Q value at pH 4.13 and 8.00, for podand 1, Hg2+ was the highest rejected cation by

this podand with Q value 3.43 ± 0.07 at pH 8.00, with 72.88 ± o.61, Fig (8). Fig (9) shows the maximum Q value at pH 4.13 and 8.00, for podand 2, Hg2+ was the highest rejected cation by this podand with Q value 4.01 ± 0.08 at pH 8.00, with 85.25 ± o.73, Fig (10). Also Fig (11) shows the maximum Q value at pH 4.13 and 8.00, for podand 3, Hg2+ was the highest rejected cation by this podand with Q value 3.52± 0.06 at pH 8.00, with 74.75± o.64, Fig (12). Fig (13) shows the maximum Q value at pH 4.13 and 8.00, for podand 4, also Hg2+ was the highest rejected cation by this podand with Q value 3.33 ± 0.06 at pH 8.00, with 70.66± o.62, Fig (14). And Fig (15) shows the maximum Q value at pH 4.13 and 8.00, for podand 5, and also Hg2+ was the highest rejected cation by this podand with Q value 3.46 ± 0.07 at pH 8.00, with 73.63± o.70 Fig (16).

However, in this study, all ions are rejected at the two pH values (4.13 and 8.0), except UO_2^{2+} which was negligible at pH 4.13 while detection was noticed clearly at pH 8.0.

The increase in percentage removal of metal ions due to increase in pH may be explained on the basis of a decrease in competition between proton (H^+) and positively charged metal ion at the surface sites and also by decrease in positive charge near the surface resulting in a lower repulsion of the adsorbing metal ions . The higher mobility of H^+ ions present, favored the preferential adsorption of hydrogen ions compared to metal ions (Jimoh, Egila, Dauda and Iyaka, 2011). This explain the low uptake of uranyl at pH 4.13 (Semiao, Rossiter and Schafer, 2010) and also low for other metal ions (Aklil, Mouflih and Sebti, 2004.; Waly, Dakroury, El-Sayed and El-Salam, 2010). This trend is not far from independent suggestion that at lower pH value, the surface of the adsorbent is surrounded by hydroxonium ions (H_3O^+), thereby preventing the metal ions from approaching the binding sites of the sorbent. (Ajmal et al. 2000). During sorption, the ions of smaller ionic radii tend to move faster to potential adsorption, similar observation had been reported by several other researchers (Mohsen, 2007.; Oboh and Aluyor, 2008.; Oyebamiji et al., 2009.; Egila et al., 2010).

Also at low pH where the majority of the nitrogen and sulfur atoms are protonated, the affinity towards the metal ions is poor, as a result, the stability of the complex is low. In case of increasing pH, the affinity and stability of the podand-metal complexes increase (Trivunac and Stevanovic, 2006.; Barakat, 2008).

Since Cu(II) is influenced by pH to a greater extent than other studied cations (Malandrino, Abollino, Giacomino, Aceto and Mentasti, 2006), we studied its complexation at pH 6.7 which was choosen according to a diagram of solubility of metal hydroxide as a function of pH (Viguri, Andre´s, Iban˜ez, Ruiz Puente, Irabien, 2000), to avoid hydroxide precipitation of Cu(II).

On the other hand, the determination of complex structure, and donor sites in the podand which is responsible for the formation of bonds with metal can be accomplished by NMR –spectrometer, elemental analysis and IR- spectrophotometer (Raman, Raja and Sakthivel, 2007.; Tan and Ang, 1988). Which was beyond the aim of this work.

4.3. Effect of contact time.

By increasing the contact time between metal ions and podands, tables 4, 5 and 12, we noticed an increase in the retention percentages of the heavy metal ions studied up to a maximum capacity at 4h; depending on the podand and metal cations. Stirring of 8-48 h practically does not improve the metal retention by podands. Which means that the podands were saturated at C T 4h or before.

4.4. Effect of temperature on the drying of coated filter papers

Tables 7 and 9 illustrate the Cf for podands 3 and 4 respectively with different drying temperatures (25-80 oC) at pH 4.13, and Tables 8 and 10 illustrate the Cf for podand 3 and 4 respectively with different drying temperatures (25-80 oC) at pH 8.00. There is no significant difference shown in range of drying temperatures (25-80 oC), which means no effect on the cohesive forces between filter paper and the podand. By contrast, there is a finite decrease in mass of coated podand, which may result from leaching of the podands through the filter paper by increasing temperature. However, the filter paper begin to convert to crisp brown feature at higher temperatures (> 80 ^{o}C).

4.5. Effect of podand structure

4.5.1. End group

When exchange the amide group instead of ester group in podands 1 and 5, there is no change in the trend of complexation with metals as compared together, except between Cu2+ and Ni2+, this may be due to Ni2+ is considered hard cation, have stronger interaction with three N-atom of bridge group and amide group.

4.5.2. Bridge group

In podands 1-4, they have the same ester end group, but they differ in their bridge group. the trend of cations retention was for Podand 1 / Hg2+ > Zn2+ > Cu2+ > Ni2+ > Co2+ > UO22+ . Podand 2 / Hg2+ > Cu2+ > Zn2+ > Co2+ > Ni2+ > UO22+ . Podand 3 / Hg2+ > Cu2+ > Zn2+ > Ni2+ > Co2+ > UO22+ . Podand 4 / Hg2+ > Cu2+ > Zn2+ > Ni2+ > UO22+ > Co2+, with two exceptions, the first one was in podand 1, switch between Cu2+ and Zn2+ as compared with others, where Zn2+ rejection was more than Cu2+, this may be due to Cu2+ is considered soft cation, has stronger interaction with podands 2, 3 and 4, which have S-atoms in

their bridge group. The second exception was in podand 4, switch between UO22+ and Co2+, as compared with others, when central S-atom in bridge group of podand 3 was displaced by O-atom in bridge group of podand 4, also, this modification lead to increasing the rejection of UO22+ and Ni2+ cations, while the others, their rejections were non developed, and there is no clear explanation.

Table 1
Structure of the synthesized podands

Podand #	Podand Structure	Ref
1		(Mizyed and Ashram, 2011)
2		(Ashram, 2002)
3		(Ashram, 2002)
4		(Al-Jarrah. 2006)
5		(Mizyed and Ashram, 2011)

Table 2

Removal efficiency (R_{em}) values for heavy metals with podands 1-5, at pH 8.00.

Podand #	$UO2^{2+}$	Zn^{2+}	Cu^{2+}	Co^{2+}	Ni^{2+}	Hg^{2+}
1	38.75 ± 1.85	72.75 ± 0.33	71.13 ± 0.43	62.38 ± 0.90	67.00 ± 0.45	72.88 ± 0.99
2	41.25 ± 1.19	64.13 ± 0.45	75.88 ± 0.45	66.50 ± 0.70	69.00 ± 0.45	85.50 ± 0.38
3	50.33 ± 0.39	70.81 ± 0.54	72.53 ± 0.56	57.24 ± 0.44	62.91 ± 0.48	74.75 ± 0.58
4	57.41 ± 0.92	69.20 ± 1.11	69.69 ± 1.12	53.76 ± 0.86	66.65 ± 1.07	70.66 ± 1.13
5	39.63 ± 1.35	73.13 ± 0.82	65.00 ± 0.65	59.75 ± 0.99	69.50 ± 0.82	73.75 ± 1.39

Table 3

Final concentration (C_f) for compound 1 at pH 4.13 and pH 8.00, C T is 8h.

Metal	C_o (ppm)	C_f (ppm)	
		pH= 4.13	pH = 8
UO_2^{2+}	8.00	8.00 ± 0.00	4.91 ± 0.15
Zn^{2+}	8.00	5.93 ± 0.04	2.19 ± 0.03
Cu^{2+}	8.00	6.21 ± 0.04	2.32 ± 0.03
Co^{2+}	8.00	6.42 ± 0.06	3.01 ± 0.07
Ni^{2+}	8.00	6.13 ± 0.03	2.65 ± 0.04
Hg^{2+}	8.00	6.31 ± 0.03	2.17 ± 0.08

Table 4

Final concentration (C_f) for compound 1 at different contact time and pH 8.00.

Cation	C_o (ppm)	C_f (ppm) C T (h)			
		4	8	24	48
UO_2^{2+}	8.00	4.92 ± 0.08	4.91 ± 0.15	4.90 ± 0.02	4.90 ± 0.03
Zn^{2+}	8.00	2.24 ± 0.02	2.19 ± 0.03	2.18 ± 0.01	2.18 ± 0.01
Cu^{2+}	8.00	2.32 ± 0.03	2.32 ± 0.03	2.31 ± 0.01	2.31 ± 0.01
Co^{2+}	8.00	3.05 ± 0.05	3.01 ± 0.07	3.01 ± 0.01	3.01 ± 0.02
Ni^{2+}	8.00	2.68 ± 0.03	2.65 ± 0.04	2.64 ± 0.02	2.64 ± 0.01
Hg^{2+}	8.00	2.21 ± 0.07	2.17 ± 0.08	2.17 ± 0.02	2.17 ± 0.02

Table 5

Final concentration (C_f) for compound 2 at pH 4.13 and pH 8.00, C T is 8h.

Cation	C_o (ppm)	C_f (ppm) pH= 4.13	pH = 8
UO_2^{2+}	8.00	8.00 ± 0.00	4.71 ± 0.10
Zn^{2+}	8.00	6.35 ± 0.02	2.88 ± 0.04
Cu^{2+}	8.00	6.04 ± 0.04	1.94 ± 0.04
Co^{2+}	8.00	7.45 ± 0.06	3.17 ± 0.06
Ni^{2+}	8.00	6.17 ± 0.04	3.48 ± 0.04
Hg^{2+}	8.00	5.74 ± 0.03	1.18 ± 0.03

Table 6

Final concentration (C_f) for compound 2 at different contact time and pH 8.00.

Cation	C_o (ppm)	C_f (ppm) C T (h) 4	8	24	48
UO_2^{2+}	8.00	4.75 ± 0.10	4.71 ± 0.10	4.70 ± 0.02	4.70 ± 0.03
Zn^{2+}	8.00	2.91 ± 0.03	2.88 ± 0.04	2.87 ± 0.01	2.87 ± 0.01
Cu^{2+}	8.00	1.99 ± 0.02	1.94 ± 0.04	1.93 ± 0.01	1.93 ± 0.01
Co^{2+}	8.00	3.20 ± 0.05	3.17 ± 0.06	3.16 ± 0.02	3.16 ± 0.02
Ni^{2+}	8.00	3.51 ± 0.02	3.48 ± 0.04	3.48 ± 0.01	3.48 ± 0.01
Hg^{2+}	8.00	1.21 ± 0.03	1.18 ± 0.03	1.16 ± 0.01	1.16 ± 0.01

Table 7

Final concentration (C_f) for compound 3 at pH 4.13 and different drying temperatures .

Cation	C_o (ppm)	C_f (ppm) 25 °C	50 °C	80 °C
UO_2^{2+}	8.00	7.87 ± 0.10	7.87 ± 0.01	7.87 ± 0.01
Zn^{2+}	8.00	6.56 ± 0.02	6.58 ± 0.01	6.58 ± 0.01
Cu^{2+}	8.00	6.13 ± 0.02	6.15 ± 0.02	6.15 ± 0.02
Co^{2+}	8.00	6.27 ± 0.02	6.29 ± 0.01	6.29 ± 0.01
Ni^{2+}	8.00	6.92 ± 0.02	6.93 ± 0.02	6.93 ± 0.01
Hg^{2+}	8.00	7.22 ± 0.03	7.23 ± 0.03	7.23 ± 0.03

Table 8

Final concentration (C_f) for compound 3 at pH 8.00 and different drying temperatures .

Cation	C_o (ppm)	C_f (ppm) 25 ^oC	50 ^oC	80 ^oC
UO_2^{2+}	8.00	3.92 ± 0.09	3.97 ± 0.03	3.97 ± 0.03
Zn^{2+}	8.00	2.26 ± 0.04	2.34 ± 0.05	2.34 ± 0.03
Cu^{2+}	8.00	2.12 ± 0.03	2.20 ± 0.01	2.20 ± 0.01
Co^{2+}	8.00	3.36 ± 0.05	3.42 ± 0.03	3.42 ± 0.03
Ni^{2+}	8.00	2.90 ± 0.04	2.97 ± 0.04	2.97 ± 0.02
Hg^{2+}	8.00	1.94 ± 0.04	2.02 ± 0.05	2.02 ± 0.02

Table 9

Final concentration (C_f) for compound 4 at pH 4.13 and different drying temperatures.

Cation	C_o (ppm)	C_f (ppm) 25 ^oC	50 ^oC	80 ^oC
UO_2^{2+}	8.00	7.63 ± 0.07	7.64 ± 0.06	7.64 ± 0.06
Zn^{2+}	8.00	6.67 ± 0.04	6.86 ± 0.01	6.71 ± 0.01
Cu^{2+}	8.00	6.15 ± 0.05	6.20 ± 0.04	6.20 ± 0.04
Co^{2+}	8.00	6.08 ± 0.04	6.13 ± 0.03	6.13 ± 0.03
Ni^{2+}	8.00	6.36 ± 0.03	6.59 ± 0.03	6.40 ± 0.04
Hg^{2+}	8.00	6.76 ± 0.03	6.79 ± 0.02	6.79 ± 0.02

Table 10

Final concentration (C_f) for compound 4 at pH 8.00 and different drying temperatures.

Cation	C_o (ppm)	C_f (ppm) 25 ^oC	50 ^oC	80 ^oC
UO_2^{2+}	8.00	3.28 ± 0.08	3.41 ± 0.08	3.41 ± 0.08
Zn^{2+}	8.00	2.31 ± 0.05	2.46 ± 0.05	2.46 ± 0.04
Cu^{2+}	8.00	2.27 ± 0.06	2.42 ± 0.04	2.42 ± 0.04
Co^{2+}	8.00	3.58 ± 0.04	3.70 ± 0.07	3.70 ± 0.05
Ni^{2+}	8.00	2.52 ± 0.03	2.67 ± 0.07	2.67 ± 0.04
Hg^{2+}	8.00	2.19 ± 0.05	2.35 ± 0.02	2.35 ± 0.02

Table 11

Final concentration (C_f) for compound 5 at pH 4.13 and pH 8.00, C T is 8h.

Cation	C_o (ppm)	C_f (ppm)	
		pH= 4.13	pH = 8
UO_2^{2+}	8.00	7.85 ± 0.10	4.83 ± 0.11
Zn^{2+}	8.00	5.83 ± 0.06	2.15 ± 0.07
Cu^{2+}	8.00	6.08 ± 0.12	2.81 ± 0.05
Co^{2+}	8.00	6.11 ± 0.08	3.22 ± 0.08
Ni^{2+}	8.00	6.10 ± 0.04	2.44 ± 0.07
Hg^{2+}	8.00	6.52 ± 0.09	2.11 ± 0.11

Table 12

Final concentration (C_f) for compound 5 at different contact time and pH 8.00 .

Cation	C_o (ppm)	C_f (ppm) C T (h)			
		4	8	24	48
UO_2^{2+}	8.00	4.84 ± 0.12	4.83 ± 0.11	4.83 ± 0.13	4.83 ± 0.12
Zn^{2+}	8.00	2.16 ± 0.05	2.15 ± 0.07	2.15 ± 0.05	2.15 ± 0.06
Cu^{2+}	8.00	2.83 ± 0.09	2.81 ± 0.05	2.80 ± 0.11	2.80 ± 0.10
Co^{2+}	8.00	3.25 ± 0.11	3.22 ± 0.08	3.22 ± 0.06	3.22 ± 0.05
Ni^{2+}	8.00	2.44 ± 0.08	2.44 ± 0.07	2.44 ± 0.07	2.44 ± 0.06
Hg^{2+}	8.00	2.13 ± 0.10	2.11 ± 0.11	2.10 ± 0.11	2.10 ± 0.11

4.6. Comparison between our results and related literature

According to R_{em} in our study and in literature, the trend of our results agree in general with those using inorganic and organic sorbents, however, our results showed less removal percent which means that the podands are poor ligands.

Calcined phosphate (Aklil, Mouflih and Sebti, 2004), zeolite 4A (Hui, Chao and Kot, 2005), alumina (Cervera, Arnal and Guardia, 2003) and cement kiln dust (Waly, Dakroury, El-Sayed and El-Salam, 2010), are examples of inorganic sorbents which have the same trend for a selected metals, also organic sorbent such as: triazine drived macrocycle adsorb Hg^{2+} and Cu^{2+} as highest cations (Pourghobadi et al, 2000), and this agree with most of crown ethers (Gasemi and Shamsipur, 1996), Insoluble starch xanthate (Wing, Doane and Russell, 1975.; Kim and Lee, 1999), chitosan

(Cervera, Arnal and Guardia, 2003) and carboxy methyl cellulose (Barakat and Schmidt, 2008) as organic sorbent.

For UO_2^{2+} the results showed less effect in detection, than those of tannic acid and gallic acid, which at pH 10 and 11 where adsorption increased from 20% up to 100%, although some other acidic ligands adsorb 2% of $UO2^{2+}$ at pH 3 which increases to 70% at pH 10 (Semião, Rossiter and Schäfer, 2010).

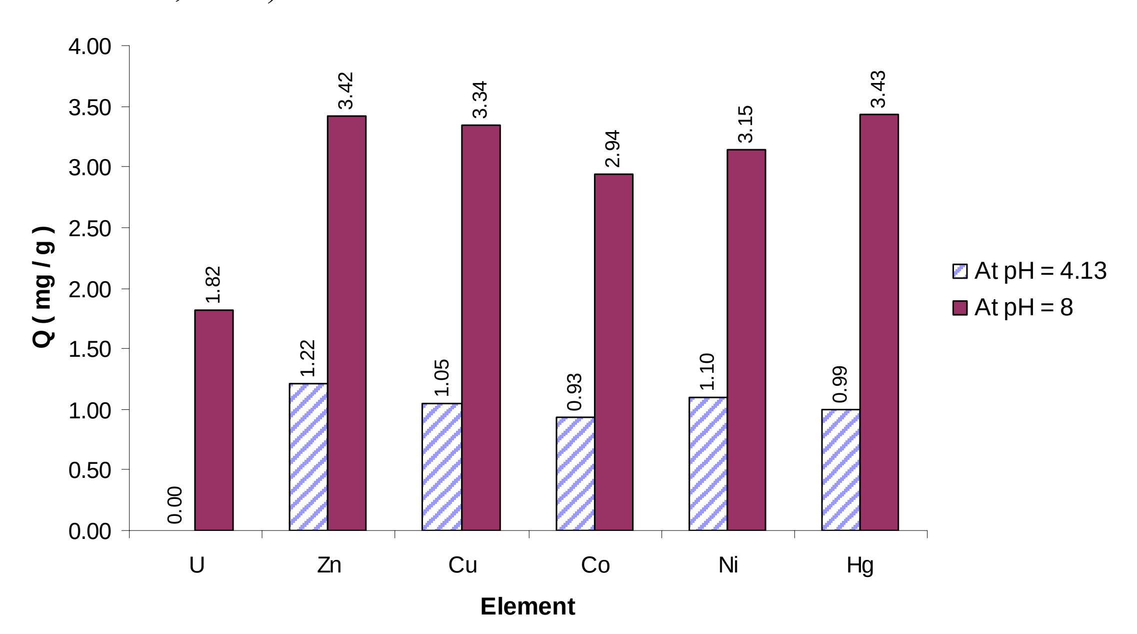


Fig 7 .
Adsorptive capacity Q (mg metal / g adsorpent), at different pH for compound **1** .

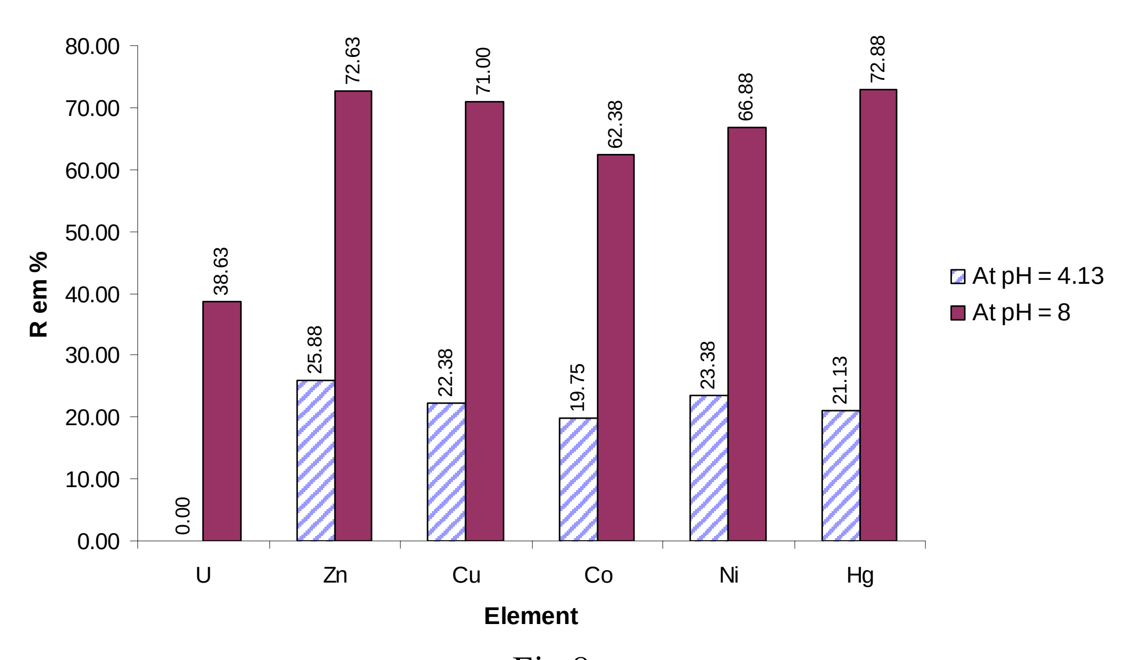


Fig 8 .
Percentage removal (R_{em}) of metal, at different pH for copmound **1**

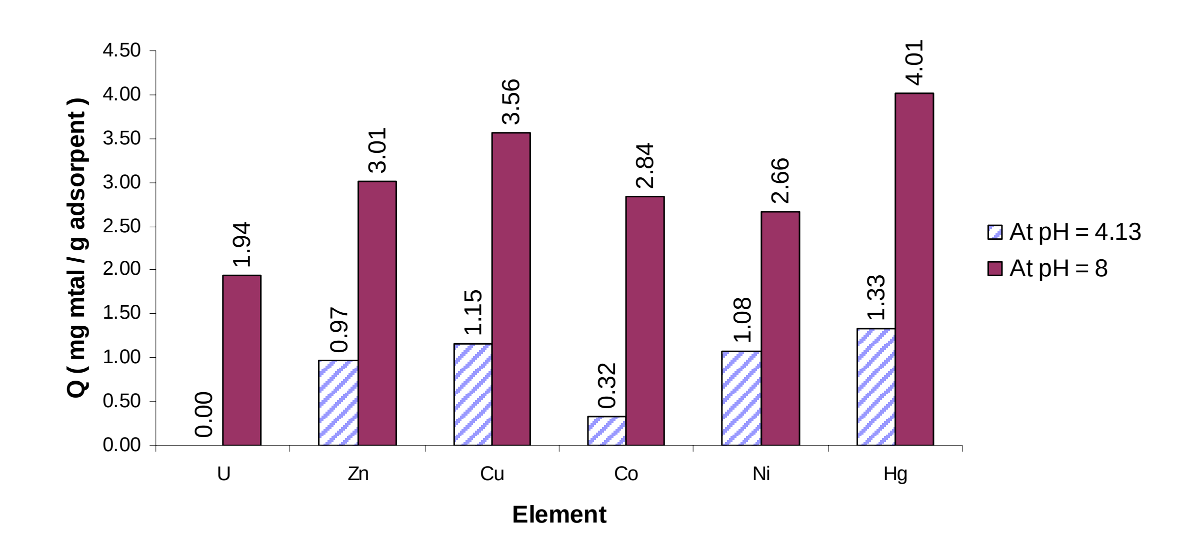


Fig 9.
Adsorptive capacity Q (mg metal/g adsorpent), at different pH for compound **2**

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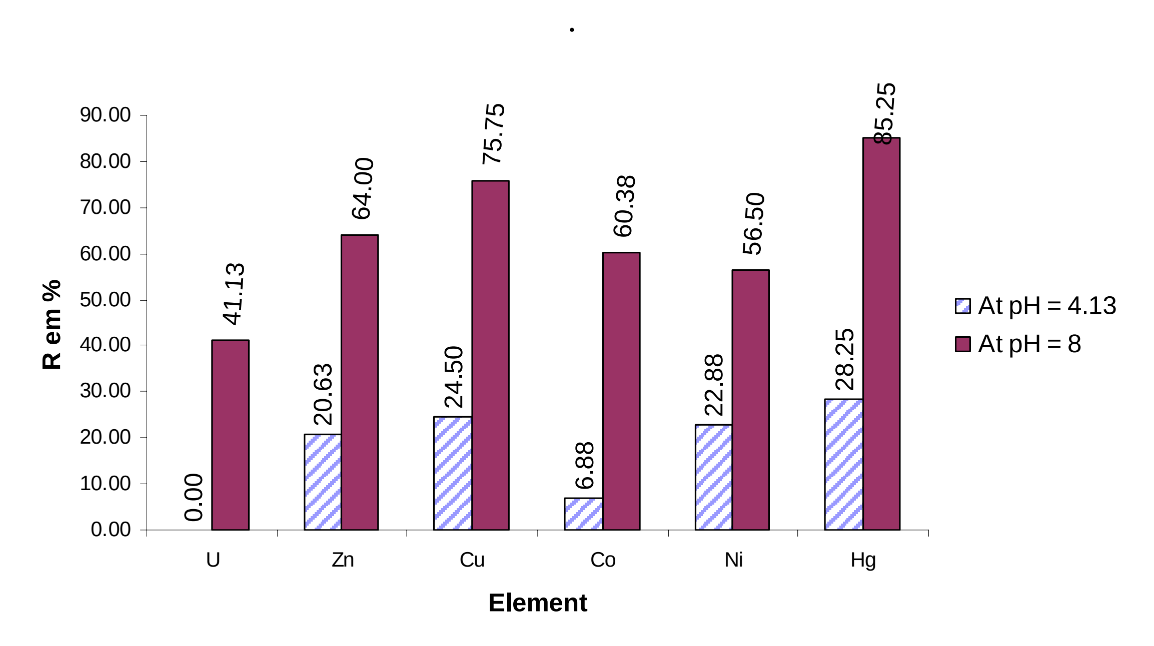


Fig 10
. Percentage removal (R_{em}) of metal, at different pH for copmound **2** .

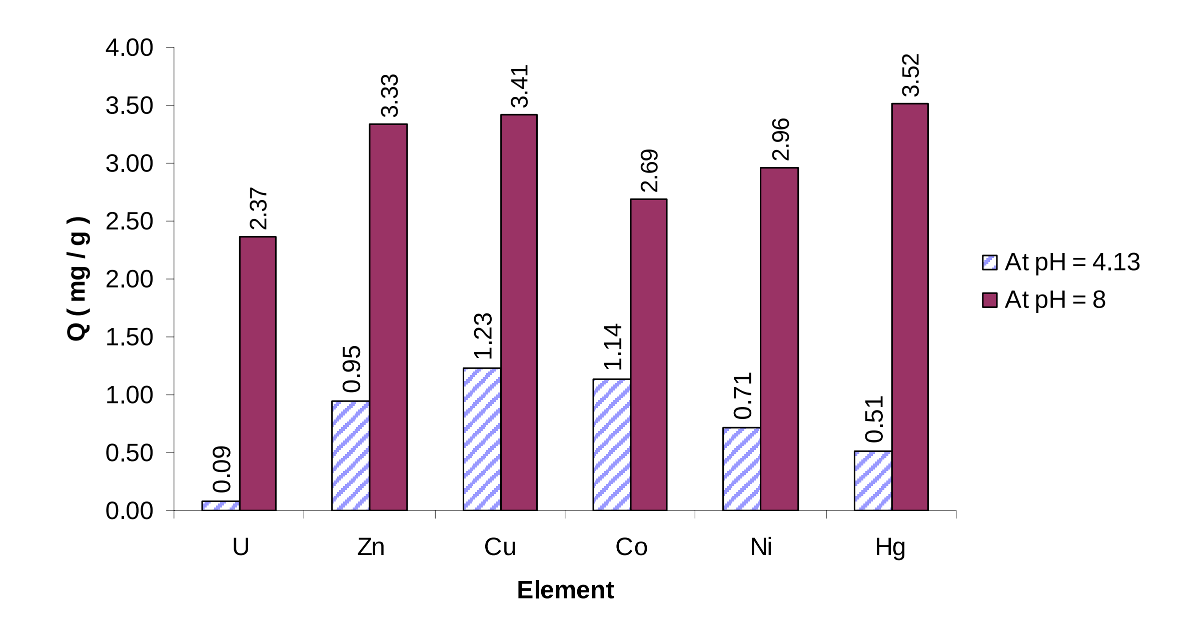


Fig 11 .
Adsorptive capacity Q (mg metal / g adsorpent), at different of pH for compound **3** .

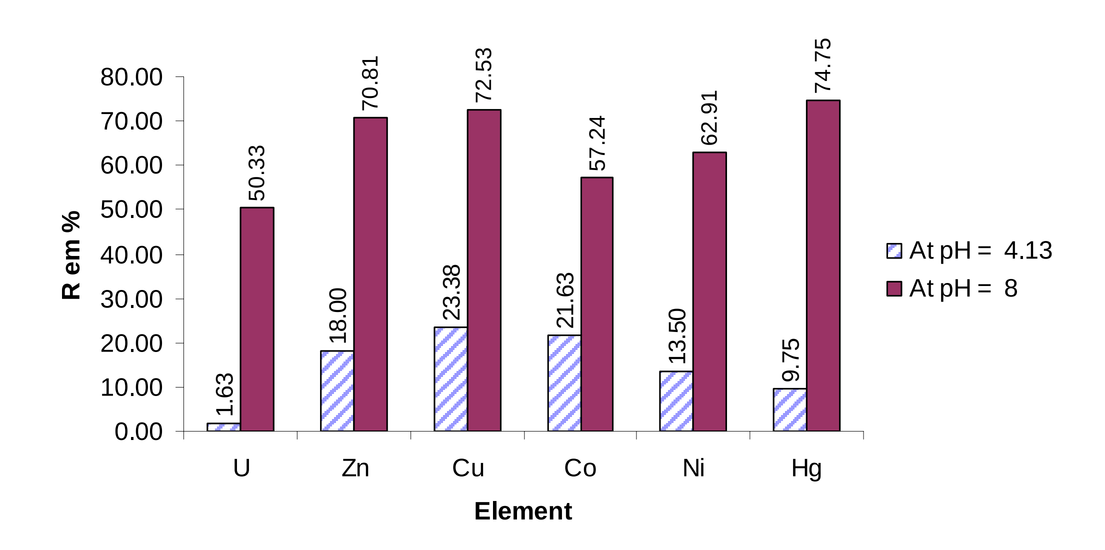


Fig 12 .
Percentage removal (R_{em}) of metal, at different of pH for compound **3** .

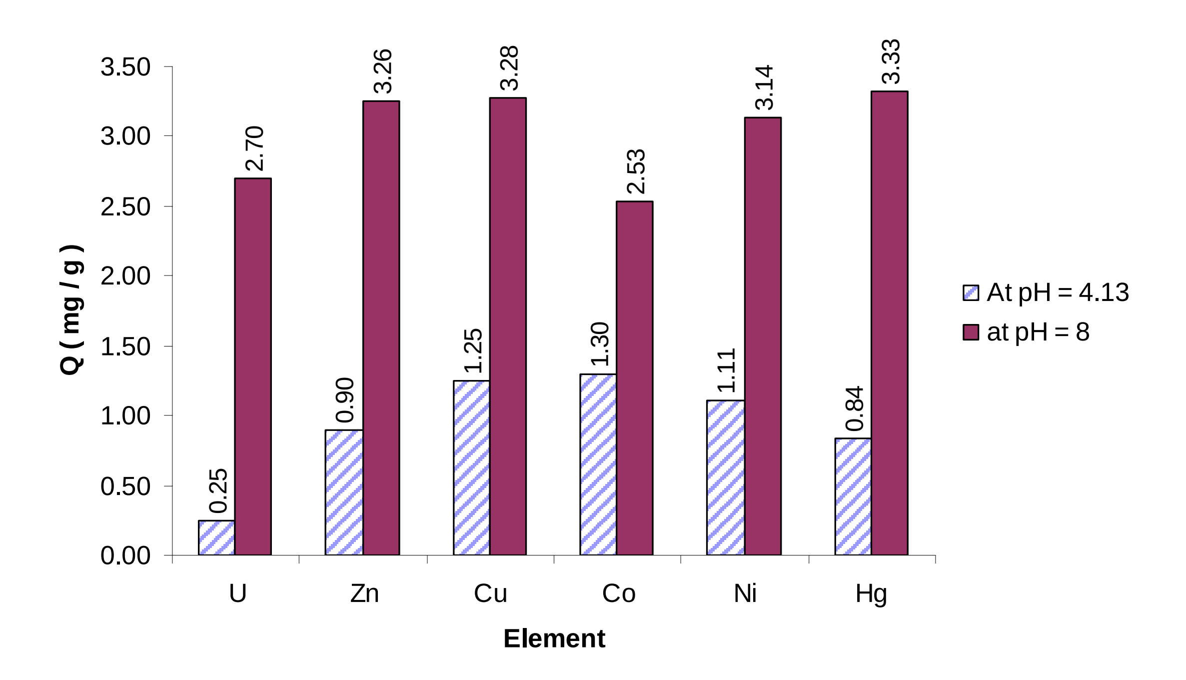


Fig 13 .
Adsorptive capacity Q (mg metal / g adsorpent), at different pH for compound **4** .

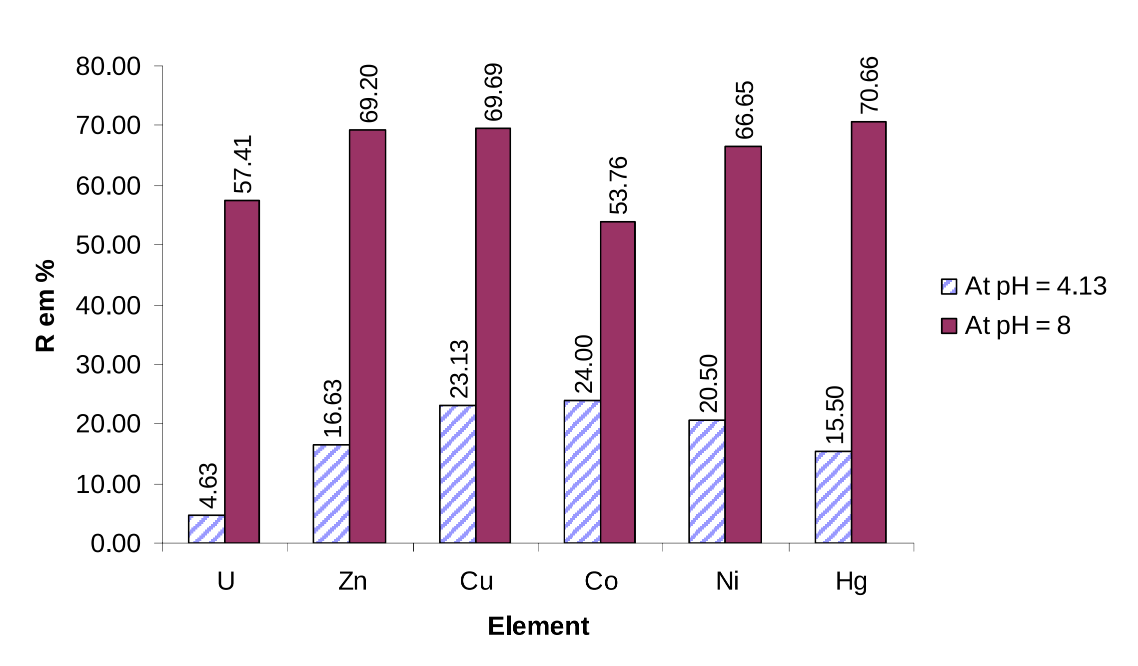


Fig 14 .
Percentage removal (R_{em}) of metal, at different pH for compound **4** .

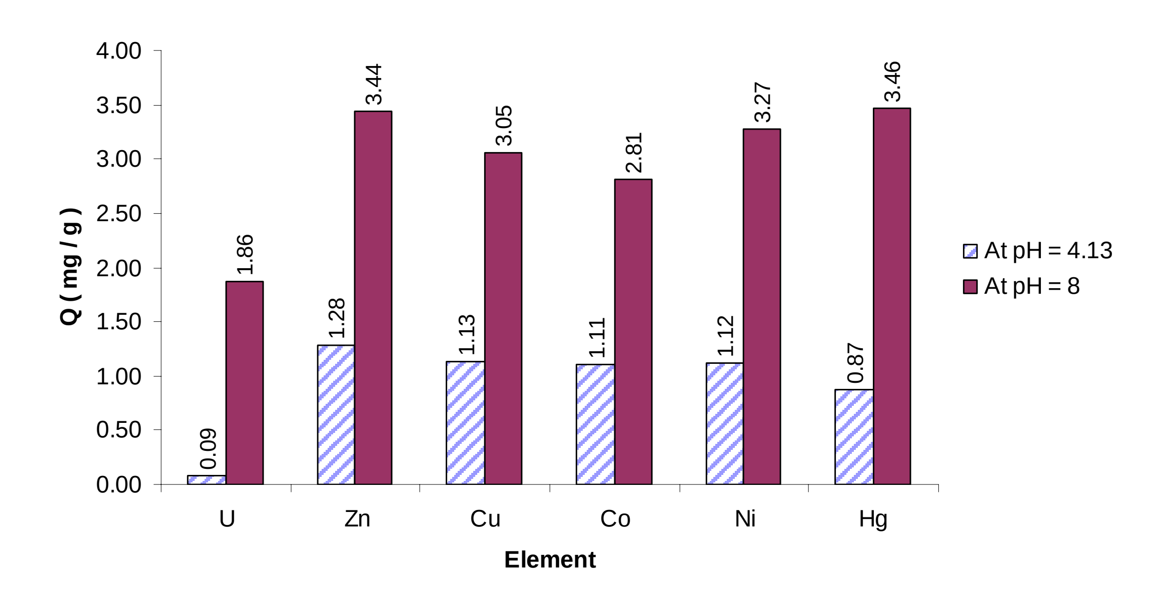


Fig 15 .
Adsorptive capacity Q (mg metal / g adsorpent), at different pH for compound **5** .

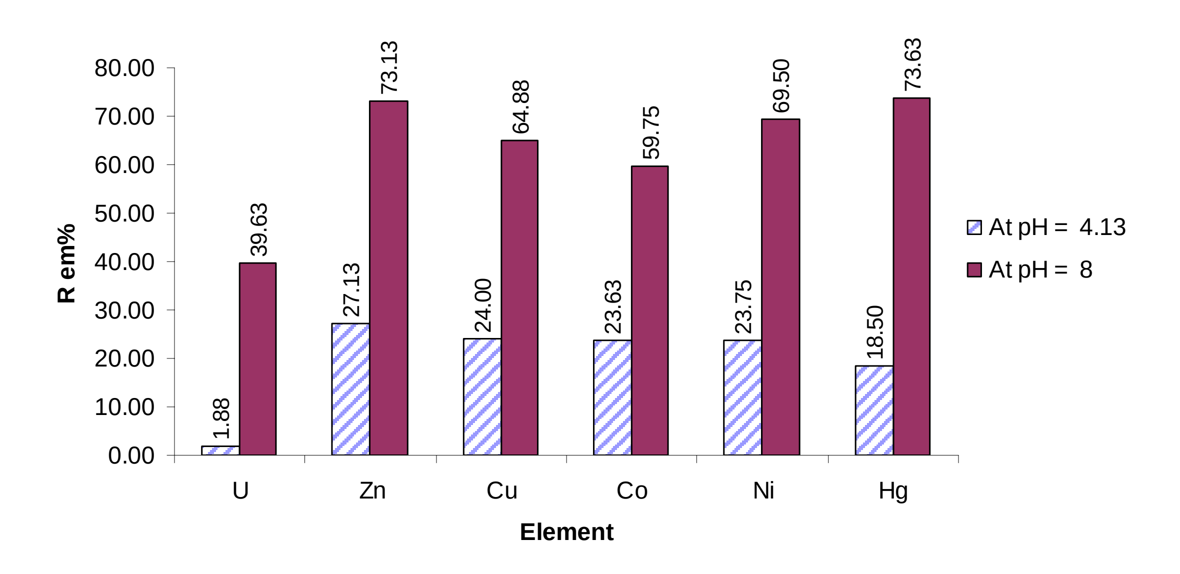


Fig 16 .
Percentage removal (R_{em}) of metal, at different pH for copmound **5** .

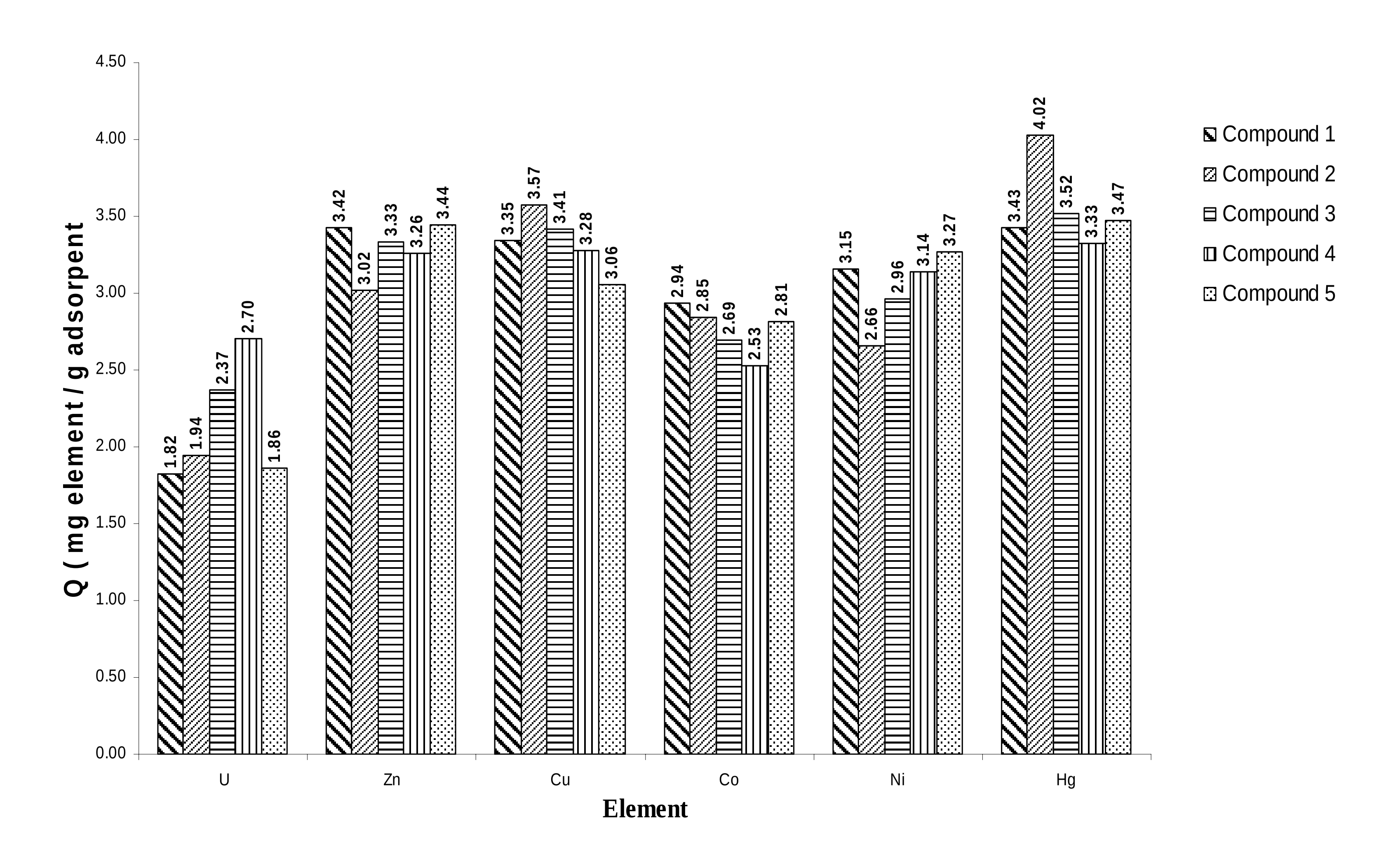


Fig 17 . Comparison of Q values of each metal for podands (1 -5) at pH = 8 and contact time is 48 for solid and semi-solid podands (1, 2, 5).

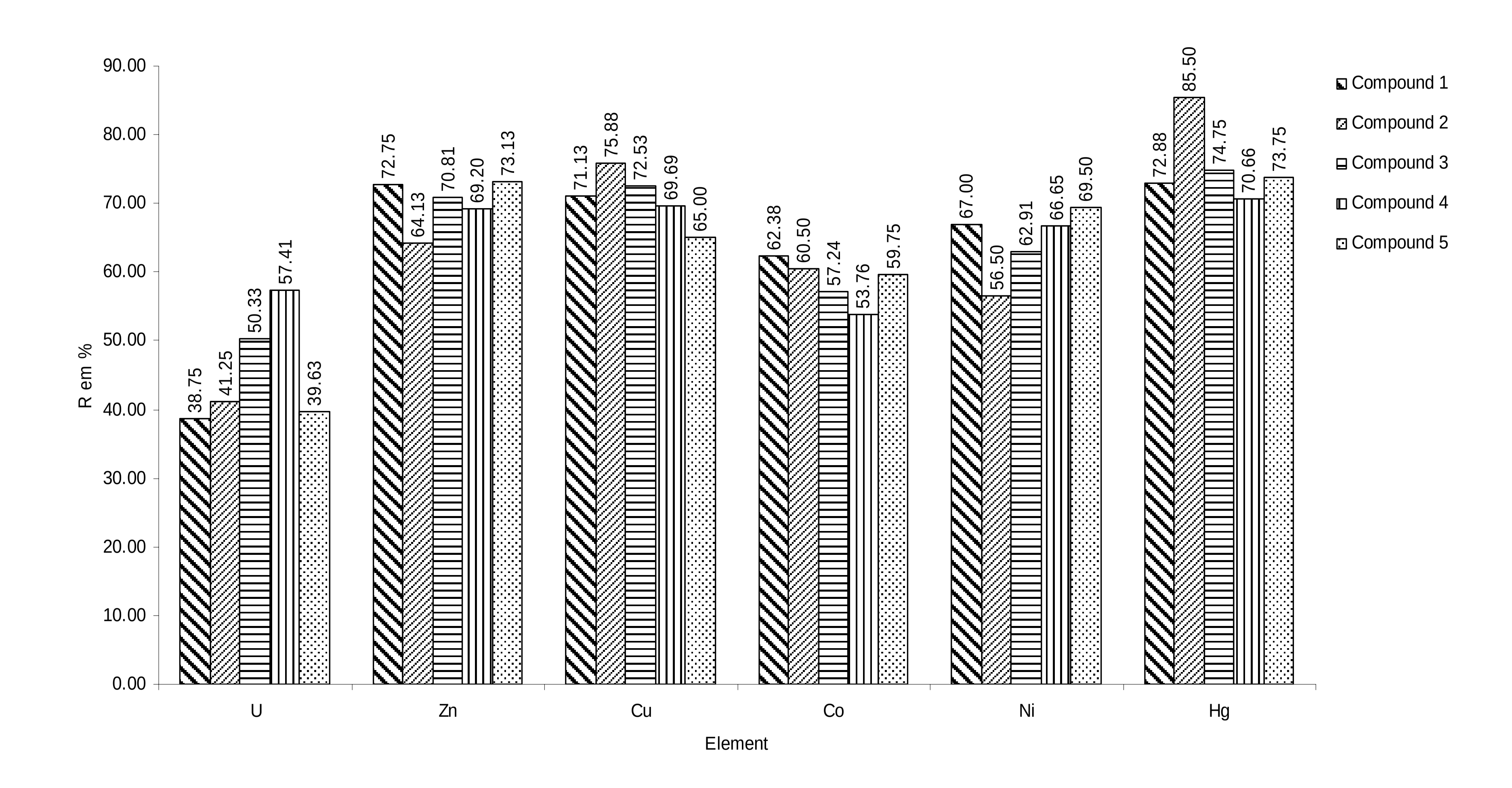


Fig 18 . Comparison of R_{em} values of each metal for podands (1 -5) at pH = 8 and contact time is 48 for solid and semi-solid podands (1, 2, 5).

4.7. Conclusions and Recommendations

Podands can be used to detect some metals in alkaline pH solutions to avoid H^+ interferences. Every podand showed relative affinity to a certain metals, this may be due to the sizes of podands and types of bridge atoms (S, N and O). In general, Hg^{2+} and Cu^{2+} were the highest adsorbed cations, $Zn^{2+}$and Ni^{2+} were moderately adsorbed cations, Co^{2+} and UO_2^{2+} were the lowest adsorbed cations.

The contact time was not a main factor in this study after 4h. In coating filter paper case, the difference in drying temperature was not a factor in adsorption of studied metals.

Comparing the R_{em} values of the studied podands to other literature's organic and inorganic adsorbents, our podands are considered as poor ligands in detecting the studied metals.

Suggestion for future work, include synthesis of more substituted podands to adsorb heavy metals more effectively. The hydroxyl and carboxylic groups may be the most preferable to improve the podands ability to make complexces with metals better.

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Appendix (I)
Procedures and Schemes

All starting materials and podands were resynthesized by literature procedures as the following :

Starting Materials :

General procedur preparation of o-(Ethoxycarbonyl-methoxy)benzaldehyde a

In 250 ml two-neck flask equipped with a magnatic stirrer bar and a reflux condenser, salicylaldehyde (12.21 g, 0.1 mol) ethyl bromoacetate (16.7 g, 0.1 mol) and anhydrous K_2CO_3 (13.8 g, 0.1 mol) were mixed in anhydrous acetone (150 ml). The mixture was refluxed for 3-4 h and then allowed to cool to room temperature. The product was extracted by diethyl ether and washing with 5% NaOH followed by water until the aqueous washes were neutral to pH paper. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to give oily product which crystallized after few hours as a pale yellow solid in 90% (mp 39-40 ^oC) (Ashram, 2002).

General procedur Preparation of 2-chloro-N,N-diethylacetamide d .

In 500 ml two-neck flask equipped with a magnatic stirrer bar, which found in ice-salt bath. diethylamine (11 g, 0.15 mol) and 20% NaOH (150 ml) were mixed in dichloromethane (150 ml), until the temperature reach to ($^-18$ - $^-25$ ^oC). Chloroacetylchloride (16.94 g, 0.15 mol) was added to the cold mixture along five min, the reaction time was 25 – 30 min, separation of organic layer then the solvent was removed in vacuo. Oily colorless product was obtained in quantitative yield. (Mizyed and Ashram, 2011).

General procedur preparation of o-(N,N-diethylcarbonylmethoxy benzaldehyde) e

In 500 ml two-neck flask equipped with a magnatic stirrer bar and a reflux condenser, salicylaldehyde (18.32 g, 0.15 mol) 2-chloro-N,N-diethylacetamide **d** (22.44 g, 0.15 mol) KI (25 g, 0.15 mol) and anhydrous K_2CO_3 (20.7 g, 0.15 mol) were mixed in anhydrous acetonitril (150 ml). The mixture was refluxed for 2.5 - 3 h, and then allowed to cool to room temperature. KI and K_2CO_3 were filtered from the reaction mixtyre, the solvent was removed in vacuo, and the crud product was dissolved in $CHCl_3$ and washed with 5% NaOH followed by water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to give orange-yellow oily product in 73-75% . (Mizyed and Ashram, 2011).

General procedur preparation of o-(Ethoxycarbonylmethoxy) benzyl alcohol **f** **.**

To a solution of **a** (31.23 g, 0.15mol) in MeOH (50 ml) was added $NaBH_4$ (5.67 g, 0.15 mol) at -5 – 0 ^oC. the reaction was stirred for 15 min and then queched by adding 10 ml of cold water , followed by aqueous 5% HCl until the solution become acidic to pH paper. The mixture was extracted with $CHCl_3$. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to give **f** as colorless oil in 95% yield. (Mizyed and Ashram, 2011).

General procedur preparation of o-(Ethoxycarbonyl methoxy)benzyl chloride **g** **.**

To a solution of **f** (31.5 g, 0.15 mol) in dry C H_2Cl_2 (200 ml) at 0 ^oC was added freshly distilled $SOCl_2$ (22.38 g, 13.66 ml, 0.3 mol). The reaction mixture was stirred at 0 ^oC for 15 min and then was quenched by adding 50 ml of cold water. The organic layer was washed with water until the aquoeus layer was nutral to pH paper. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to give **g** as a pale yellow oil in 90-92%yield. (Mizyed and Ashram, 2011).

General procedur preparation of *Podands*, 1 , 5 by Schiff base reaction.

Schiff's base podands were prepared by condensation reaction of ethylenediamine or diethylenetriamine with the corresponding aldyhyde in a molar ratio 1 : 2, respectively, in ethanol solvent at reflux temperature. For compound **1**, ethylenediamine (1.5 g, 0.025 mol) and compound **a** (10.4 g, 0.05 mol). For compound **5** ethylenediamine (1.5 g, 0.025 mol) and compound **e** (11.75 g, 0.05 mol). The reaction was stirred for 3-4 h. The solvent was evaporated under vacue using rotary evaporator to give **1** as yellow solid in 80% (mp 76 -78 ^oC), **5** as pale yellow semi solid in 80% . The ^1H- and ^{13}C-NMR, IR analysisand elemental analysis measured for the products are consistent very well with the corresponding Schiff's base formula. (Ha, Ong, Win, Koh and Yeap, 2008.; Tan and Ang, 1988.; Naeimi, Safari and Heidarnezhad, 2007.; Raman, Raja and Sakthivel, 2007.; Mizyed and Ashram, 2011).

Preparation of final products *(Podands)*. 2 , 3 , 4 .

Preparation of Compound 2 .

A compound **8** (5.72 g, 0.025 mol), K_2CO_3 (3.45 g, 0.025 mol) and ethanedithiol (1.18 g, 0.0125 mol) in CH_3CN (100 ml) at reflux temperature. The reaction was left to stir for 3-4 h. Then the mixture was filtered. The filtrate was added to $CHCl_3$ (100 ml) and then washed with

water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to give **2** as a colorless solid in quantitative yield. (mp 74-75 ^oC). (Ashram, 2002).

Preparation of Compound 3 .

A compound **g** (5.72 g, 0.025 mol), K_2CO_3 (3.45 g, 0.025 mol) and mercaptoethyl sulfide (1.93 g, 0.0125 mol) in CH_3CN (100 ml) at reflux temperature. The reaction was left to stir for 3-4 h. Then the mixture was filtered. The filtrate was added to $CHCl_3$ (100 ml) and then washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to give **3** as a colorless oil in quantitative yield. (Ashram, 2002).

Preparation of Compound 4 .

A compound **g** (5.72 g, 0.025 mol), K_2CO_3 (3.45 g, 0.025 mol) and 2-mercaptoethyl ether (1.73 g, 0.0125 mol) in CH_3CN (100 ml) at reflux temperature. The reaction was left to stir for 3-4 h. Then the mixture was filtered. The filtrate was added to $CHCl_3$ (100 ml) and then washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to give **4** as a yellow-orange oil in quantitative yield. (Ashram, 2002).

Complexation Study .

Coating Compound 3 and 4 on filter paper.

In about 10 ml of acetone, each compound **3** and **4** were dissolved separately in two plastic petrri dishs. Three weighted cleaned filter papers (Whatman No 1, 7.0 cm) were immersed in this solution for 5 min, and dried at different temperaturs (25, 50 and 80 ^oC). Then reweight to calculate the weight of the podand which was between 0.072-0.076 g. (Ackerman and Hurtubise. 2002).

preparation of starting materials and podands.

Stage I : The preparation of *o-(Ethoxycarbonylmethoxy)benzaldehyde* **a**. (Scheme 1) .
Stage II – A : The preparation of *2-chloro-N,N-diethylacetamide* **d** (Scheme 2)
Stage II – B : The preparation of *o-(N,N-diethylcarbonylmethoxy-benzaldehyde* . **e** (Scheme 3) .
Stage III : The preparation of *Podands* by Schiff base reaction . **1** , **5** . (Scheme 4)
Stage IV : The Preparation of *o-(Ethoxycarbonylmethoxy) benzyl alcohol*. **f** . (Scheme 5) .
Stage V : The preparation of *o-(Ethoxycarbonylmethoxy)benzyl chloride*. **g** . (Scheme 6) .
Stage VI : The preparation of final products (Podands) . **2** , **3** , **4** . (Scheme 7) .

preparation of o-(Ethoxycarbonylmethoxy)benzaldehyde **a** from reaction of salicylaldehyde with bromoethylacetate. (Scheme 1).

CHO, OH → ($BrCH_2CO_2C_2H_5$; K_2CO_3 / Reflux 3h) → CHO, O, $CO_2C_2H_5$

a

Scheme 1

Preparation of *2-chloro-N,N-diethylacetamide* **d** from reaction of chloroacetylchloride with diethylamine **c** . (Scheme 2) .

O, Cl, Cl + Et_2NH → (NaOH , CH_2Cl_2; -25 C^o) → O, Cl, N, Et, Et

b **c** **d**

Scheme 2

Preparation of *o-(N,N-diethylcarbonylmethoxy benzaldehyde* **e** from reaction of salicylaldehyde with **d** . (Scheme 3) .

K_2CO_3 , KI , CH_3CN

Reflux 3h

d **e**

Scheme 3

Preparation of *Podands* by Schiff base reaction. (Scheme 4) .

a **Y : OEt**
e **Y : N(Et)$_2$**

1 **Y : OEt**
5 **Y : N(Et)$_2$**

Scheme 4

Preparation of *o-(Ethoxycarbonylmethoxy) benzalcohol* **f** by reduction of **a** . (Scheme 5) .

$NaBH_4$ / CH_3OH

0 C^o

a **f**

Scheme 5

preparation of *o-(Ethoxycarbonylmethoxy)benzylchloride* **g** by reaction of **f** with thionylchloride . (Scheme 6) .

$SOCl_2$ / CH_2Cl_2

Scheme 6

Preparation of final products ***(Podands).*** **2** , **3** , **4** .

K_2CO_3 / CH_3CN

Reflux 3h

Scheme 7